Ionic and Covalent Bonds in CeO2 Crystal (STATES AND STRUCTURES - Atomic and Molecular Physics)

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Hirohide Nakamatsu and Takeshi Mukoyama

We have performed cluster calculations to study the bonding nature in the CeO_2 crystal, using the relativistic discrete-variational Xα method. The electron charge distribution of CeO_2 is compared with those of ZrO_2 and CaF_2. The charge density in the metal atomic region indicates stronger covalency for CeO_2 than that in Zr for ZrO_2. The repulsion between the metal and oxygen ionic cores is, however, strong and superior to the covalent interaction, and thus the ionic character determines the static bonding nature in the CeO_2 crystal. Mixed interaction due to the independent ionic and covalent contributions arises from the ionic Ce 5s, 5p and covalent Ce 4f, 5d orbitals which are proximate to each other in the bond region.

Keywards: Bond nature/ Lanthanoid/ ZrO_2 / CaF_2 / Relativisitc electronic structure/ Dirac-Fock-Slater method

Like alkaline earth metals, lanthanoids have a primary character of hard ionic spheres in solutions and insulators. In particular, 4f orbitals were not considered to be a participant in chemical bonding because they are smaller in size than the filled 5p orbitals and the 4f energy bands of compounds are generally narrow due to a small ligand field. Contrary to typical ionic behavior, the 4f and 5d orbitals of lanthanoids are considered to participate significantly in covalent bonding according to the electronic structure calculations. Koelling et al. deduced the presence of f and d covalent bonding in CeO_2 and PrO_2 from band calculations(1).

Gschneidner has shown that the 4f electron concentration in the bonding is estimated to be about 0.7 of an electron for light lanthanoids by an analysis of the melting point and heat of sublimation for the metals(2). A summary of the experimental work concerning the participation of 4f orbitals in the chemical bonding is presented in Ref. 2. Photoelectron spectra and X-ray absorption spectra indicate 4f participation in the bonding of Ce compounds. However, the relation between the analyzed covalent character and the typical ionic behavior in insulator materials has not been clearly revealed.

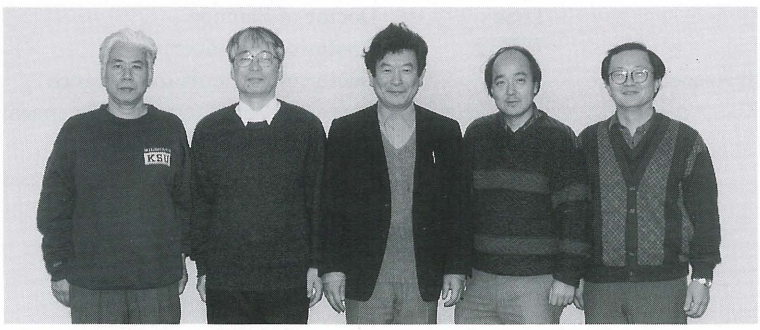
In the present work(3), relativistic DV-Xα calculations for CeO_2, CaF_2 and ZrO_2 compounds have been performed to clarify the ionic bond and the covalent one due to the lanthanoid 4f and 5d orbitals.

Relativistic calculations are indispensable to the study of the electronic structure of molecules containing heavy elements. It has been shown that relativistic effects play a substantial role in the chemical

STATES AND STRUCTURES —Atomic and Molecular Physics —

Scope of research

In order to obtain fundamental information on the property and the structure of materials, the electronic states of atoms and molecules are investigated in detail using X-ray, SR, ion beam from accelerator and nuclear radiation from radioisotopes. Theoretical analysis of the electronic states and development of new radiation detectors are also performed.



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bonding of atoms with an atomic number greater than 50(4). In particular, the f orbitals in question are remarkably changed in energy and spatial distribution due to the relativistic effect(5). In the present work, we performed relativistic DV-Xα calculations based on the Dirac-Fock-Slater method and the cluster model was used for compounds.

The electron charge density calculated for the clusters is examined. The charge densities of valence bands with O 2p and F 2p as the main components are studied since the covalent interaction appears in these bands. The other occupied bands make small contributions to the covalent bonding. The metal ions share the charge density of the O 2p and F 2p valence bands according to the covalency. For CaF_2, a typical ionic compound, the F 2p component essentially determines the charge distribution and the contribution from the Ca component is negligibly small. The peak at the Ca nucleus is present but its radially integrated quantity within the atomic sphere is negligible. In the case of ZrO_2, which is considered to have a strong covalent character among the various types of metal oxides, a large contribution of the Zr orbitals to the "O 2p band" is clarified in this charge density plot. For CeO_2, the participation of the Ce orbitals into the valence state is found to be remarkable and the metal atom component is greater than that of the Zr oxides. The covalent interaction between the Ce and O ions produces the charge density for the Ce 4f and 5d orbitals in the O 2p band. The charge density in the interatomic region around r= 2au is lower for CeO_2 than that for ZrO_2, though the charge density inside the Ce atom is larger than that inside Zr.

A precise examination of the charge density in the interatomic region and the population analysis lead to the conclusion that the ionic bonding is the determinant of the chemical bonding in CeO_2 at the equilibrium interatomic distance even though the covalency is strong in the sense of orbital participation in forming the valence state. These independent ionic and covalent interactions arise from the ionic 5s, 5p and covalent 4f and 5d orbitals which are proximate to each other with respect to the energy and amplitude of the wavefunction in the bond region.

The ionic and covalent characteristics have been investigated by observing the charge density distribution for the valence bands of CaF_2 and ZrO_2. For CeO_2, the charge density in the bond region between the Ce and O atoms is almost equal to that of the ideal ion. This implies that the Ce and O atoms are joined with the ionic bond, whereas the charge density within the Ce atomic region indicates a stronger covalent interaction than that for ZrO_2. This *mixed interaction* due to the independent ionic and covalent contributions arises from the Ce 5s, 5p, 4f and 5d orbitals which are proximate to each other in the bond region. The components of Ce 5s, 5p make a repulsive interaction with O 2p because of overlap of the essentially filled orbitals. Concerning the bonding in CeO_2, this repulsion cancels the covalent bonding between Ce 4f, 5d and O 2p. The present result mentioned is valid at the equilibrium interatomic distance.

The effective charges of the Ce and O ions are notably reduced owing to the covalent interaction, but they do not reflect the strength of the actual covalent bond which lies in the interatomic region on the bond axis. In contrast to CeO_2, for most of the insulator compounds consisting of light elements including some transition metals, the deviation of the effective charge from that of the ideal ion can be a useful measure of the charge density contributing to the covalent bonding. This measure postulates that the overlap between two hybrid orbitals is enough to characterize the covalent bonding. In a simple case, the hybrid orbital of each atom consists of a single atomic orbital. Actually, the bonding in ZrO_2 is characterized by a pair of Zr 4d and O 2p. They effectively make a covalent contribution to the bond. In the case of CeO_2, several kinds of Ce valence orbitals are concerned with the bonding characteristics and form an *overlap complex* where various kinds of independent orbital overlaps are significant. This really includes a direct overlap of the ionic cores which produces the repulsive interaction. The effective charge of the Ce ion is small relative to the formal charge, because both the Ce 4f and 5d orbitals participate in sharing the charge in the valence bands. Moreover, the Ce 5s, 5p components cause the repulsion of the ionic cores and are the determinant of the dominant ionic nature.

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